Supporting information for:

Coupled Quasidiabatic Potential Energy Surfaces for LiFH

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Additional files:

StrategyA.dat: ASCII file containing the MRDCI energies calculated with the Strategy A thresholds for the ground state of LiFH. The fitted (surface fit J) ground-state energies are also tabulated.

StrategyB.dat: ASCII file containing the MRDCI energies calculated with the Strategy B thresholds for the ground state and first-excited state of LiFH. The fitted (surface fit J) energies are also tabulated.

StrategyC.dat: ASCII file containing the MRDCI energies calculated with the Strategy C thresholds for six lowest energy states of LiFH. The

fitted (surface fit J) energies for the two lowest energy states are also tabulated.

JacobiB.dat: ASCII file containing the MRDCI energies calculated with the Strategy B thresholds for six lowest energy states of LiFH. These additional calculations were performed along three one-dimesional cuts through the minimum of the van der Waals well of the ground electronic state.

LiFHJ.f ASCII file containing the FORTRAN program for the LiFH potential energy matrix, surface fit J.

LiFHJS.f ASCII file containing the FORTRAN program for the LiFH potential energy matrix, surface fit JS.

Note: See POTLIB-online[1] for a convenient way to download either of the potential energy matrix routines.

1. Nucler geometry grids for the *ab initio* calculations

1.1. Strategy A data

The 6-root MRDCI calculations employing the largest thresholds T, i.e., $T = 4, 6,$ and 8 μE_h, (Strategy A) consisted of 3,380 geometries. In specifying grids we will use a shorthand notation that, for example, 2.5(0.1)2.8 denotes 2.5, 2.6, 2.7, and 2.8. The main grid included 27 Li–F distances: $r_{LiF} = 2.0, 2.25, 2.5, 2.7(0.1)2.9, 2.9553, 3.0(0.1)4.0,$ 4.25, 4.5, 5.0(1.0)7.0, and 9.0(2.0)15.0 a_0; 24 H–F distances: $r_{HF} = 1.2(0.2)1.6, 1.7,$ 1.7325, 1.8(0.1)3.0, 3.25(0.25)4.0, 5.0, and 7.0 a_0; and five values of the Li–F–H angle: θ = 45, 70(20)110, and 179.99 degrees. Notice the presence of the equilibrium bond lengths for LiF ($r_{LiF} = 2.9553$ a_0) and HF ($r_{HF} = 1.7325$ a_0) among the values of r_{LiF} and r_{HF}, respectively. This grid of 3,240 points was augmented by calculations for $\theta = 0.01$ degrees, $r_{LiF} = 3.0(2.0)7.0, 11.0,$ and 15.0 a_0, and $r_{HF} = 1.2, 1.4(0.1)1.8,$ and 2.0(0.2)2.4 a_0, and by calculations for $r_{HF} = 3.8$ a_0, $r_{LiF} = 2.25, 2.5, 2.7(0.1)2.9, 2.9553, 3.0(0.1)4.0,$ 4.25, and 4.5 a_0, and $\theta = 45, 70(20)110,$ and 179.99 degrees.

1.2. Strategy B data

For the 2-root MRDCI calculations employing the intermediate thresholds T, i.e., $T = 1, 2,$ and 3 μE_h (Strategy B), the main grid consisted of 27 Li–F distances and five values of the Li–F–H angle identical to those described above, and of up to 18 H–F distances, covering the intervals 1.4–3.0 a_0 for $\theta = 45$ degree, 1.4–2.7 a_0 for $\theta = 70, 90,$ and 110 degrees, and 1.4–2.5 a_0 for $\theta = 179.99$ degrees. This grid of 2,052 geometries was augmented by two sets of extra calculations. In the first set of extra calculations, we added 45 points for $\theta = 0.01$ degrees, using the following grid: $r_{LiF} = 3.0(2.0)7.0, 11.0,$ and 15.0 a_0, and $r_{HF} = 1.2, 1.4(0.1)1.8,$ and 2.0(0.2)2.4 a_0. In the second set of extra calculations, which played an important role in fine tuning the final fit, we added 135 nuclear geometries obtained by combining the 27 Li–F distances from the main grid with the following values of r_{HF} and θ: $r_{HF} = 2.7$ a_0 and $\theta = 179.99$ degrees, and $r_{HF} = 3.0$ a_0 and $\theta = 70, 90, 110,$ and 179.99 degrees. The total number of Strategy B geometries is 2,232, and these geometries form a subset of the Strategy A geometries.

1.3. Strategy C data

Finally, the most accurate, 1-root calculations using the smallest selection thresholds $T = 0.15$, 0.30, and 0.45 μE_h (Strategy C) were performed on a grid of 15 Li–F distances: $r_{LiF} = 2.5$, 2.8, 2.9553, 3.0(0.2)4.0, 4.25, 4.5, 5.0, and 7.0(4.0)15.0 a_0, ten H–F distances: $r_{HF} = 1.4$, 1.6, 1.7, 1.7325, 1.8, 2.0, 2.1, and 2.2(0.2)2.6 a_0, and seven values of the Li–F–H angle: $\theta = 45$, 70(20)150, and 179.99 degrees. This grid of 1,050 points was augmented by 24 extra points for $\theta = 0.01$ degrees, $r_{LiF} = 5.0$ and 7.0(4.0)15.0 a_0, and $r_{HF} = 1.5(0.1)1.8$, 2.0, and 2.2 a_0 (to improve the description of the $\theta = 0$ region) and by adding 11 values of θ for $r_{LiF} = 3.6$ a_0 and $r_{HF} = 1.763$ a_0, i.e., $\theta = 10(10)60$, 80(30)140, 160, and 170 degrees, to improve the description of the θ-dependence. To further improve the description of the saddle point region and obtain a highly accurate description of the product channel (including the shallow minimum in the product valley and the LiF + H asymptote), we added 90 points corresponding to $r_{HF} = 2.5$, 2.9553, 3.2, 3.4, and 3.8 a_0, $r_{HF} = 2.8$, 3.0, 3.25, 3.5, 4.0, and 5.0 a_0, and $\theta = 45$, 70, and 90 degrees, 140 points corresponding to $r_{LiF} = 2.5$, 2.9553, 3.2, 3.4, and 3.8 a_0, $r_{HF} = 6.0$, 7.0(2.0)15.0, and 20.0 a_0, and $\theta = 45$, 70, 90, and 179.99 degrees, and 47 points corresponding to $r_{HF} = 3.8$ a_0, $r_{LiF} = 2.25 - 5.0$ a_0, and $\theta = 45$, 70(20)110, and 179.99 degrees. The total number of points used in the MRDCI calculations for the ground state with Strategy C calculations was 1,362.

1.4. Additional calculations

An additional 45 calculations were performed using the Strategy B thresholds (i.e., $T = 1$, 2, and 3 μE_h) for the six lowest-energy states of LiFH. The calculations were performed along three one-dimensional cuts through the minimum of the ground state van der Waals well: $q_{HF} = 1.76327$ a_0, $Q_{Li,HF} = 2.5(0.2)3.3$, 3.59757, 3.7, 4.0(0.5)5.0, 6.0, 8.0, 11.0, 15.0 a_0, and $\chi_{Li,HF} = 70.01$ degrees; $q_{HF} = 1.76327$ a_0, $Q_{Li,HF} = 3.59757$ a_0, and $\chi_{Li,HF} = 1$, 10(10)60, 70.01, 80(10)170, 179 degrees; and $q_{HF} = 1.3(0.1)1.7$,

1.76327, 1.9(0.1)2.4, 2.7, 3.0 a_0, $Q_{Li,HF}$ = 3.59757 a_0, and $\chi_{Li,HF}$ = 70.01 degrees, where q_{HF} is the magnitude of the vector from H to F ($\mathbf{q}_{HF}$), $Q_{Li,HF}$ is the magnitude of the vector from Li to the center-of-mass of HF ($\mathbf{Q}_{Li,HF}$), and $\chi_{Li,HF}$ and is angle between $\mathbf{Q}_{Li,HF}$ and $\mathbf{q}_{HF}$.

2. Quasidiabatic potential energy matrix for LiFH: Surface fit J

2.1. LiFH U_{11} surface

The U_{11} potential energy surface explicitly contains long-range interactions in the Li(2s) + HF asymptote as a correction to the interaction potential

$$U_{11}(\mathbf{R}) = U_{11}^{\mathrm{I}}(\mathbf{R}) + U_{11}^{\mathrm{LR}}(\mathbf{R}), \tag{1}$$

where $\mathbf{R} = (r_{\mathrm{LiH}}, r_{\mathrm{HF}}, r_{\mathrm{LiF}})$, and r_{AB} is the A–B internuclear distance. The long-range forces U_{11}^{LR} are described in Sec. 2.4. The interaction potential U_{11}^{I} contains only the Li + HF asymptote and the product van der Waals well. It is relatively simple and may be described by the sum of three diatomic terms,

$$U_{11}^{\mathrm{I}}(\mathbf{R}) = S_{\mathrm{LiH}}(\mathbf{R}) + S_{\mathrm{HF}}(\mathbf{R}) + S_{\mathrm{LiF}}(r_{\mathrm{LiF}}) + D_{\mathrm{HF}}^{\mathrm{e}}, \tag{2}$$

where S_{AB} represents the AB diatomic interaction, and $D_{\mathrm{HF}}^{\mathrm{e}}$ sets the zero of energy.

The LiH diatomic does not represent the isolated Li–H interaction. It represents Li–H interactions in the close presence of F and is purely repulsive,

$$S_{\mathrm{LiH}}(\mathbf{R}) = S_{\mathrm{LiH}}^{\mathrm{a}}(r_{\mathrm{LiH}}) + [S_{\mathrm{LiH}}^{\mathrm{c}}(r_{\mathrm{LiH}}) - S_{\mathrm{LiH}}^{\mathrm{a}}(r_{\mathrm{LiH}})]\Phi_{\mathrm{LiH}}(\mathbf{R}), \tag{3}$$

$$S_{\mathrm{LiH}}^{\mathrm{a}}(r_{\mathrm{LiH}}) = D_{\mathrm{LiH}}^{\mathrm{a}} \exp[-\beta_{\mathrm{LiH}}^{\mathrm{a}}(r_{\mathrm{LiH}} - r_{\mathrm{LiH}}^{0})], \tag{4}$$

$$S_{\mathrm{LiH}}^{\mathrm{c}}(r_{\mathrm{LiH}}) = D_{\mathrm{LiH}}^{\mathrm{c}} \exp[-\beta_{\mathrm{LiH}}^{\mathrm{c}}(r_{\mathrm{LiH}} - r_{\mathrm{LiH}}^{0})], \tag{5}$$

where Φ_{LiH} is a switching function given by

$$\Phi_{\mathrm{LiH}}(\mathbf{R}) = \frac{1}{2} - \frac{1}{2}\tanh\left(\frac{r_{\mathrm{LiH}}^{\mathrm{x}}(\mathbf{R}) - \rho_{\mathrm{LiH}}}{\Delta_{\mathrm{LiH}}}\right), \tag{6}$$

$$r_{\mathrm{LiH}}^{\mathrm{x}} = r_{\mathrm{LiH}} - r_{\mathrm{LiF}} + \gamma_{\mathrm{LiH}}r_{\mathrm{HF}}. \tag{7}$$

The HF potential curve S_{HF} was fit to experimental Rydberg-Klein-Rees (RKR) data for the HF molecule.[2] The functional form is a Morse curve with a range parameter that depends on the HF bond length,

$$S_{\mathrm{HF}}^{\mathrm{e}}(r_{\mathrm{HF}}) = D_{\mathrm{HF}}^{\mathrm{e}} X_{\mathrm{HF}}^{\mathrm{e}}(r_{\mathrm{HF}})[X_{\mathrm{HF}}^{\mathrm{e}}(r_{\mathrm{HF}}) - 2], \tag{8}$$

where

$$X_{HF}^{e}(r_{HF}) = \exp[-\beta_{HF}^{e}(r_{HF})(r_{HF} - r_{HF}^{e})] \tag{9}$$

and

$$\beta_{HF}^{e}(r_{HF}) = b_{HF}^{0} + b_{HF}^{1}(r_{HF} - r_{HF}^{0}) + b_{HF}^{2}(r_{HF} - r_{HF}^{0})^{2}. \tag{10}$$

Additional flexibility was added in the interaction region such that

$$S_{HF}(\mathbf{R}) = S_{HF}^{c}(\mathbf{R}) + [S_{HF}^{e}(r_{HF}) - S_{HF}^{c}(\mathbf{R})]\Phi_{HF}(r_{LiF}), \tag{11}$$

where

$$S_{HF}^{c}(\mathbf{R}) = D_{HF}^{c}(\mathbf{R})X_{HF}^{c}(r_{HF})[X_{HF}^{c}(r_{HF}) - 2], \tag{12}$$

$$X_{HF}^{c}(r_{HF}) = \exp[-\beta_{HF}^{c}(r_{HF} - r_{HF}^{c})], \tag{13}$$

$$D_{HF}^{c}(\mathbf{R}) = D_{HF}^{e} - [D_{HF}^{cc} + \tfrac{1}{2}D_{HF}^{chi}(1 - \cos\chi_{Li,HF})], \tag{14}$$

$$\Phi_{HF}(r_{LiF}) = \frac{1}{2} + \frac{1}{2}\tanh\left(\frac{r_{LiF} - \rho_{HF}}{\Delta_{HF}}\right), \tag{15}$$

and $\chi_{Li,HF}$ is the Jacobi angle, i.e., the angle between the vector from the Li atom to the center of mass of HF ($\mathbf{Q}_{Li,HF}$) and the vector from H to F ($\mathbf{q}_{HF}$). The Jacobi vector $\mathbf{Q}_{Li,HF}$ depends on the masses of the H and F nuclei, and these masses (along with the mass of Li as discussed below) are therefore parameters of the fit. The masses are taken as those of the most abundant isotopes and are listed in Table 1.

The LiF diatomic $S_{LiF}(r_{LiF})$ is a shallow Morse curve,

$$S_{LiF}(r_{LiF}) = D_{LiF}X_{LiF}(r_{LiF})[X_{LiF}(r_{LiF}) - 2], \tag{16}$$

$$X_{LiF}(r_{LiF}) = \exp[-\beta_{LiF}(r_{LiF} - r_{LiF}^{0})]. \tag{17}$$

The values of the parameters used in the U_{11} potential matrix element are given in Table 1.

2.2. LiFH U_{12} coupling surface

The diabatic scalar coupling U_{12} is described by

$$U_{12}(\mathbf{R}) = U_{12}^0(\mathbf{R})\Phi_{12}(r_{HF}), \tag{18}$$

where $U_{12}^0(\mathbf{R})$ is a physically motivated functional form that is cut off for large values of r_{HF} where the excited-state potential energy surface becomes energetically inaccessible, i.e.,

$$\Phi_{12}(r_{HF}) = \frac{1}{2} - \frac{1}{2}\tanh[(r_{HF} - \rho_{12})/\Delta_{12}]. \tag{19}$$

Nonadiabatic transitions in this regions are unimportant and eliminating the off-diagonal coupling in these regions greatly reduces the expense of accurate quantum mechanical dynamics calculations.

As discussed in Secs. II and III of the main paper, we calculated the diabatic coupling for the isolated LiH and LiF diatoms. The coupling between the two states considered here vanishes for the isolated HF diatom. We therefore treat the diabatic coupling in the full system as arising from diatomic terms in the LiF and LiH bond distances,

$$U_{LiH}(r_{LiH}) = g_{LiH}(r_{LiH}/r_{LiH}^0)^6 \exp[-6(r_{LiH}/r_{LiH}^0 - 1)], \tag{20}$$

$$U_{LiF}(r_{LiF}) = g_{LiF}(r_{LiF}/r_{LiF}^0)^8 \exp[-8(r_{LiF}/r_{LiF}^0 - 1)]. \tag{21}$$

These are functions which are zero when the diatomic distances r_{LiX} (X = H, F) are zero, and increase in magnitude to a maximum of g_{LiX} at $r_{LiX} = r_{LiX}^0$ as r_{LiX} increases. For larger values of r_{LiX} the functions decrease in magnitude at a rate determined by exponential.

The magnitudes of isolated diatomic coupling terms are reduced by the approach of the remaining atom,

$$\begin{aligned} U_{12}^0(\mathbf{R}) = U_{LiH}(r_{LiH})\Phi_{HF,1}(r_{HF})\Phi_{LiF}(r_{LiF}) \\ + U_{LiF}(r_{LiF})\Phi_{HF,2}(r_{HF})\Phi_{LiH}(r_{LiH}). \end{aligned} \tag{22}$$

The functions $\Phi_{HF,1}$, Φ_{LiF}, $\Phi_{HF,2}$, and Φ_{LiH} are given by

$$\Phi_{\mathrm{HF},1}(r_{\mathrm{HF}}) = \frac{1}{2} + \frac{1}{2} \tanh \frac{r_{\mathrm{HF}} - \rho_{\mathrm{HF},1}}{\Delta_{\mathrm{HF},1}}, \tag{23}$$

$$\Phi_{\mathrm{LiF}}(r_{\mathrm{LiF}}) = \frac{1}{2} + \frac{1}{2} \tanh \frac{r_{\mathrm{LiF}} - \rho_{\mathrm{LiF}}}{\Delta_{\mathrm{LiF}}}, \tag{24}$$

$$\Phi_{\mathrm{HF},2}(r_{\mathrm{HF}}) = \frac{1}{2} + \frac{1}{2} \tanh \frac{r_{\mathrm{HF}} - \rho_{\mathrm{HF},2}}{\Delta_{\mathrm{HF},2}}, \tag{25}$$

$$\Phi_{\mathrm{LiH}}(r_{\mathrm{LiH}}) = \frac{1}{2} + \frac{1}{2} \tanh \frac{r_{\mathrm{LiH}} - \rho_{\mathrm{LiH}}}{\Delta_{\mathrm{LiH}}}. \tag{26}$$

The values of the parameters used in the U_{12} potential matrix element are given in Table 2.

2.3. LiFH U_{22} surface

The U_{22} potential energy surface explicitly contains long-range interactions in the Li($2p$) + HF and LiF + H asymptotes as a correction to the interaction potential,

$$U_{22}(\mathbf{R}) = U_{22}^{\mathrm{I}}(\mathbf{R}) + U_{22}^{\mathrm{LR}}(\mathbf{R}). \tag{27}$$

The long-range forces U_{22}^{LR} are described in Sec. 2.4. The interaction potential U_{22}^{I} is a modified[3] London-Eyring-Polanyi-Sato (LEPS)[4–6] form,

$$\begin{aligned} U_{22}^{\mathrm{I}}(\mathbf{R}) = {} & J_{\mathrm{LiH}}(\mathbf{R}) + J_{\mathrm{HF}}(\mathbf{R}) + J_{\mathrm{LiF}}(\mathbf{R}) \\ & - \frac{1}{\sqrt{2}} \sqrt{W(\mathbf{R}) + Z(\mathbf{R})^2} + D_{\mathrm{HF}}^{\mathrm{e}}, \end{aligned} \tag{28}$$

where

$$\begin{aligned} W(\mathbf{R}) = {} & (K_{\mathrm{LiH}}(\mathbf{R}) - K_{\mathrm{HF}}(\mathbf{R}))^2 + (K_{\mathrm{HF}}(\mathbf{R}) - K_{\mathrm{LiF}}(\mathbf{R}))^2 \\ & + (K_{\mathrm{LiF}}(\mathbf{R}) - K_{\mathrm{LiH}}(\mathbf{R}))^2. \end{aligned} \tag{29}$$

The functions J_{α} and K_{α} (α = LiH, HF, and LiF) are functions of diatomic singlet S_{α} and triplet T_{α} functions

$$J_{\alpha}(\mathbf{R}) = \frac{1}{2}(S_{\alpha}(\mathbf{R}) + T_{\alpha}(\mathbf{R})), \tag{30}$$

$$K_{\alpha}(\mathbf{R}) = \frac{1}{2}(S_{\alpha}(\mathbf{R}) - T_{\alpha}(\mathbf{R})). \tag{31}$$

The expression

$$Z(\mathbf{R}) = c_{2a} \exp[-c_{2b}W(\mathbf{R}) - c_{2c}(r_{HF} + r_{LiH} + r_{LiF})] \tag{32}$$

is a necessary to remove a cusp that would otherwise occur in Eq. (28) when $W(\mathbf{R})$ goes to zero.

The LiH singlet curve is the sum of two repulsive curves, one of which is present only when the LiH diatom is interacting with F,

$$S_{LiH}(\mathbf{R}) = S_{LiH}^{a}(r_{LiH}) + S_{LiH}^{c}(r_{LiH})\Phi_{LiH}(\mathbf{R}), \tag{33}$$

$$S_{LiH}^{a}(r_{LiH}) = D_{LiH}^{a2}X_{LiH}^{a}(r_{LiH})^{2} + D_{LiH}^{a1}X_{LiH}^{a}(r_{LiH}), \tag{34}$$

$$X_{LiH}^{a}(r_{LiH}) = \exp[-\beta_{LiH}^{a}(r_{LiH} - r_{LiH}^{0})], \tag{35}$$

$$S_{LiH}^{c}(r_{LiH}) = D_{LiH}^{c} \exp[-\beta_{LiH}^{c}(r_{LiH} - r_{LiH}^{0})], \tag{36}$$

$$\Phi_{LiH}(\mathbf{R}) = \frac{1}{2} - \frac{1}{2} \tanh\left(\frac{r_{LiH}^{x}(\mathbf{R}) - \rho_{LiH}}{\Delta_{LiH}}\right), \tag{37}$$

$$r_{LiH}^{x}(\mathbf{R}) = r_{LiH} - r_{LiF} + \gamma_{LiH}\, r_{HF}. \tag{38}$$

The LiH triplet is a modified anti-Morse curve,

$$T_{LiH}(r_{LiH}) = D_{LiH}^{t2}X_{LiH}^{t}(r_{LiH})^{2} + D_{LiH}^{t1}X_{LiH}^{t}(r_{LiH}), \tag{39}$$

$$X_{LiH}^{t}(r_{LiH}) = \exp[-\beta_{LiH}^{t}(r_{LiH} - r_{LiH}^{t})]. \tag{40}$$

The asymptotic HF singlet is similar to the form used for the U_{11} potential matrix element but shifted upwards by the excitation energy of Li. The singlet is cut off such that the U_{11} and U_{22} surfaces are equal at large r_{HF},

$$S_{HF}^{a}(r_{HF}) = S_{HF}^{aa}(r_{HF}) + [S_{HF}^{e}(r_{HF}) - S_{HF}^{aa}(r_{HF})]\Phi_{HF}^{a}(r_{HF}), \tag{41}$$

$$S_{HF}^{e}(r_{HF}) = D_{HF}^{e}X_{HF}^{e}(r_{HF})[X_{HF}^{e}(r_{HF}) - 2] + E_{Li(2p)}, \tag{42}$$

$$X_{HF}^{e}(r_{HF}) = \exp[-\beta_{HF}^{e}(r_{HF})(r_{HF} - r_{HF}^{e})], \tag{43}$$

$$\beta_{HF}^{e}(r_{HF}) = b_{HF}^{0} + b_{HF}^{1}(r_{HF} - r_{HF}^{0}) + b_{HF}^{2}(r_{HF} - r_{HF}^{0})^{2}, \tag{44}$$

$$S_{HF}^{aa}(r_{HF}) = D_{HF}^{aa} X_{HF}^{aa}(r_{HF})[X_{HF}^{aa}(r_{HF}) - 2], \tag{45}$$

$$X_{HF}^{aa}(r_{HF}) = \exp[-\beta_{HF}^{aa}(r_{HF})(r_{HF} - r_{HF}^{aa})], \tag{46}$$

$$\Phi_{HF}^{a}(r_{HF}) = \frac{1}{2} - \frac{1}{2}\tanh\left(\frac{r_{HF} - \rho_{HF}^{a}}{\Delta_{HF}^{a}}\right). \tag{47}$$

Additional flexibility was added to the HF singlet in the interaction region

$$S_{HF}(\mathbf{R}) = S_{HF}^{c}(\mathbf{R}) + [S_{HF}^{a}(r_{HF}) - S_{HF}^{c}(\mathbf{R})]\Phi_{HF}(r_{LiF}), \tag{48}$$

where

$$S_{HF}^{c}(\mathbf{R}) = D_{HF}^{c}(\mathbf{R}) X_{HF}^{e}(r_{HF})[X_{HF}^{e}(r_{HF}) - 2]\Phi_{HF}^{c}(r_{HF}) + E_{Li(2p)}, \tag{49}$$

$$D_{HF}^{c}(\mathbf{R}) = D_{HF}^{e} - [D_{HF}^{cc} + \frac{1}{2}D_{HF}^{chi}(1 - \cos\theta_{LiFH})], \tag{50}$$

$$\Phi_{HF}^{c}(r_{HF}) = \frac{1}{2} - \frac{1}{2}\tanh\left(\frac{r_{HF} - \rho_{HF}^{c}}{\Delta_{HF}^{c}}\right), \tag{51}$$

$$\Phi_{HF}(r_{LiF}) = \frac{1}{2} + \frac{1}{2}\tanh\left(\frac{r_{LiF} - \rho_{HF}}{\Delta_{HF}}\right), \tag{52}$$

and θ_{LiFH} is the Li–F–H bond angle.

The HF triplet contains angular dependence,

$$T_{HF}(\mathbf{R}) = T_{HF}^{0}(r_{HF})\frac{1}{2}(1 + \cos\theta_{LiFH}) + T_{HF}^{180}(r_{HF})\frac{1}{2}(1 - \cos\theta_{LiFH}), \tag{53}$$

where

$$T_{HF}^{0}(r_{HF}) = D_{HF}^{t2,0} X_{HF}^{t,0}(r_{HF})^{2} + D_{HF}^{t1,0} X_{HF}^{t,0}(r_{HF}), \tag{54}$$

$$T_{HF}^{180}(r_{HF}) = D_{HF}^{t2,180} X_{HF}^{t,180}(r_{HF})^{2} + D_{HF}^{t1,180} X_{HF}^{t,180}(r_{HF}), \tag{55}$$

$$X_{HF}^{t,0}(r_{HF}) = \exp[-\beta_{HF}^{t,0}(r_{HF} - r_{HF}^{t})], \tag{56}$$

$$X_{HF}^{t,180}(r_{HF}) = \exp[-\beta_{HF}^{t,180}(r_{HF} - r_{HF}^{t})], \tag{57}$$

The LiF singlet curve is given by

$$S_{\text{LiF}}(\mathbf{R}) = S_{\text{LiF}}^{\text{c}}(\mathbf{R}) + [S_{\text{LiF}}^{\text{a}}(\mathbf{R}) - S_{\text{LiF}}^{\text{c}}(\mathbf{R})]\Phi_{\text{LiF}}(\mathbf{R}). \tag{58}$$

The asymptotic term is based on the RKR data of Ref. 7 and on the *ab initio* data presented in Sec. II, and it is given by

$$S_{\text{LiF}}^{\text{a}}(\mathbf{R}) = \left[(D_{\text{LiF}}^{\text{e}} + E_{\text{Li}(2p)})X_{\text{LiF}}^{\text{a}}(\mathbf{R})[X_{\text{LiF}}^{\text{a}}(\mathbf{R}) - 2] + E_{\text{Li}(2p)}\right]\Phi_{\text{LiF}}^{\text{a}}(\mathbf{R}), \tag{59}$$

where

$$X_{\text{LiF}}^{\text{a}}(\mathbf{R}) = \exp[-\beta_{\text{LiF}}^{\text{a}}(\mathbf{R})(r_{\text{LiF}} - r_{\text{LiF}}^{\text{e}})], \tag{60}$$

$$\Phi_{\text{LiF}}^{\text{a}}(\mathbf{R}) = \left(\frac{1}{2} - \frac{1}{2}\tanh\frac{r_{\text{LiF}} - \rho_{\text{LiF}}^{\text{a}}}{\Delta_{\text{LiF}}^{\text{a}}}\right)\left[d_{\text{LiF}}^{\text{aa}} + (1 - d_{\text{LiF}}^{\text{aa}})\Phi_{\text{LiF}}^{\text{aa}}(r_{\text{HF}})\right], \tag{61}$$

$$\Phi_{\text{LiF}}^{\text{aa}}(r_{\text{HF}}) = \left(\frac{1}{2} + \frac{1}{2}\tanh\frac{r_{\text{HF}} - \rho_{\text{LiF}}^{\text{aa}}}{\Delta_{\text{LiF}}^{\text{aa}}}\right), \tag{62}$$

$$\beta_{\text{LiF}}^{\text{a}}(\mathbf{R}) = \beta_{\text{LiF}}^{\text{b}}(\mathbf{R})\frac{\beta_{\text{LiF}}^{\text{e}}(r_{\text{LiF}}) + \left(\frac{r_{\text{LiF}}}{\gamma_{\text{LiF}}}\right)^{n_{\text{LiF}}}}{\beta_{\text{LiF}}^{\text{b}}(\mathbf{R}) + \left(\frac{r_{\text{LiF}}}{\gamma_{\text{LiF}}}\right)^{n_{\text{LiF}}}}, \tag{63}$$

$$\beta_{\text{LiF}}^{\text{b}}(\mathbf{R}) = \beta_{\text{LiF}}^{\text{e}}(r_{\text{LiF}}) + [\beta_{\text{LiF}}^{\text{d}} - \beta_{\text{LiF}}^{\text{e}}(r_{\text{LiF}})]\Phi_{\text{LiF}}^{\text{b}}(\mathbf{R}), \tag{64}$$

$$\Phi_{\text{LiF}}^{\text{b}}(\mathbf{R}) = \left(\frac{1}{2} - \frac{1}{2}\tanh\frac{r_{\text{HF}} - \rho_{\text{LiF}}^{\text{b}}}{\Delta_{\text{LiF}}^{\text{b}}}\right)\frac{1}{2}(1 + \cos\theta_{\text{LiFH}}), \tag{65}$$

$$\beta_{\text{LiF}}^{\text{e}}(r_{\text{LiF}}) = b_{\text{LiF}}^{\text{e1}} + \frac{b_{\text{LiF}}^{\text{e2}}r_{\text{LiF}}}{\left(b_{\text{LiF}}^{\text{e3}} + b_{\text{LiF}}^{\text{e4}}r_{\text{LiF}}\right)^2}. \tag{66}$$

The form of the LiF singlet in the presence of H is

$$S_{\text{LiF}}^{\text{c}}(\mathbf{R}) = [D_{\text{LiF}}^{\text{c}}(\mathbf{R}) + E_{\text{Li}(2p)}]X_{\text{LiF}}^{\text{c}}(\mathbf{R})[X_{\text{LiF}}^{\text{c}}(\mathbf{R}) - 2], \tag{67}$$

$$D_{\text{LiF}}^{\text{c}}(\mathbf{R}) = D_{\text{LiF}}^{\text{c,0}}\frac{1}{2}(1 + \cos\theta_{\text{LiFH}}) + D_{\text{LiF}}^{\text{c,180}}\frac{1}{2}(1 - \cos\theta_{\text{LiFH}}), \tag{68}$$

$$X_{\mathrm{LiF}}^{\mathrm{c}}(\mathbf{R}) = \exp[-\beta_{\mathrm{LiF}}^{\mathrm{c}}(\mathbf{R})(r_{\mathrm{LiF}} - r_{\mathrm{LiF}}^{\mathrm{e}})], \tag{69}$$

$$\beta_{\mathrm{LiF}}^{\mathrm{c}}(\mathbf{R}) = \beta_{\mathrm{LiF}}^{\mathrm{c},0}\frac{1}{2}(1 + \cos\theta_{\mathrm{LiFH}}) + \beta_{\mathrm{LiF}}^{\mathrm{c},180}\frac{1}{2}(1 - \cos\theta_{\mathrm{LiFH}}). \tag{70}$$

The asymptotic and close forms of the LiF singlet are joined together with a switching function that incorporates angular dependence

$$\Phi_{\mathrm{LiF}}(\mathbf{R}) = \frac{1}{2} - \frac{1}{2}\tanh\frac{\rho_{\mathrm{LiF}}(\mathbf{R})}{\Delta_{\mathrm{LiF}}(\mathbf{R})}, \tag{71}$$

$$\rho_{\mathrm{LiF}}(\mathbf{R}) = (r_{\mathrm{HF}}^{\mathrm{e}} - r_{\mathrm{HF}})\cos\phi_{\mathrm{LiF}}(\mathbf{R}) - (\rho_{\mathrm{LiF}}^{\mathrm{x}}(\mathbf{R}) - r_{\mathrm{LiF}})\sin\phi_{\mathrm{LiF}}(\mathbf{R}), \tag{72}$$

$$\rho_{\mathrm{LiF}}^{\mathrm{x}}(\mathbf{R}) = \rho_{\mathrm{LiF}}^{0} + (\rho_{\mathrm{LiF}}^{180} - \rho_{\mathrm{LiF}}^{0})\frac{1}{2}(1 - \cos\theta_{\mathrm{LiFH}}), \tag{73}$$

$$\phi_{\mathrm{LiF}}(\mathbf{R}) = \phi_{\mathrm{LiF}}^{0} + (\phi_{\mathrm{LiF}}^{180} - \phi_{\mathrm{LiF}}^{0})\frac{1}{2}(1 - \cos\theta_{\mathrm{LiFH}}), \tag{74}$$

$$\Delta_{\mathrm{LiF}}(\mathbf{R}) = \Delta_{\mathrm{LiF}}^{0} + (\Delta_{\mathrm{LiF}}^{180} - \Delta_{\mathrm{LiF}}^{0})\frac{1}{2}(1 - \cos\theta_{\mathrm{LiFH}}). \tag{75}$$

The LiF triplet potential is a modified anti-Morse curve,

$$T_{\mathrm{LiF}}(\mathbf{R}) = T_{\mathrm{LiF}}^{0}(r_{\mathrm{LiF}})\frac{1}{2}(1 + \cos\theta_{\mathrm{LiFH}}) + T_{\mathrm{LiF}}^{180}(r_{\mathrm{LiF}})\frac{1}{2}(1 - \cos\theta_{\mathrm{LiFH}}), \tag{76}$$

$$T_{\mathrm{LiF}}^{0}(r_{\mathrm{LiF}}) = D_{\mathrm{LiF}}^{\mathrm{t}2,0} X_{\mathrm{LiF}}^{\mathrm{t},0}(r_{\mathrm{LiF}})^{2} + D_{\mathrm{LiF}}^{\mathrm{t}1,0} X_{\mathrm{LiF}}^{\mathrm{t},0}(r_{\mathrm{LiF}}), \tag{77}$$

$$T_{\mathrm{LiF}}^{180}(r_{\mathrm{LiF}}) = D_{\mathrm{LiF}}^{\mathrm{t}2,180} X_{\mathrm{LiF}}^{\mathrm{t},180}(r_{\mathrm{LiF}})^{2} + D_{\mathrm{LiF}}^{\mathrm{t}1,180} X_{\mathrm{LiF}}^{\mathrm{t},180}(r_{\mathrm{LiF}}), \tag{78}$$

$$X_{\mathrm{LiF}}^{\mathrm{t},0}(r_{\mathrm{LiF}}) = \exp[-\beta_{\mathrm{LiF}}^{\mathrm{t},0}(r_{\mathrm{LiF}} - r_{\mathrm{LiF}}^{\mathrm{e}})], \tag{79}$$

$$X_{\mathrm{LiF}}^{\mathrm{t},180}(r_{\mathrm{LiF}}) = \exp[-\beta_{\mathrm{LiF}}^{\mathrm{t},180}(r_{\mathrm{LiF}} - r_{\mathrm{LiF}}^{\mathrm{e}})], \tag{80}$$

The values of the parameters used in the U_{22} potential matrix element are given in Table 3.

2.4. Long-range forces

Long-range interactions[8–10] were explicitly included in the U_{11} and U_{22} surfaces as shown in Eqs. (1) and (27). The U_{11} surface contains the dipole-induced-dipole and dispersion interactions in the Li(2s) + HF arrangement,

$$U_{11}^{LR}(\mathbf{R}) = U_{11,HF}^{disp}(\mathbf{R}) + U_{11,HF}^{did}(\mathbf{R}), \tag{81}$$

where the dispersion interactions are given by the London equation,[8,9]

$$U_{11,HF}^{disp}(\mathbf{R}) = -\frac{3}{2} \frac{I_{Li(2s)} I_{HF} \alpha_{Li(2s)} \alpha_{HF}(\mathbf{R})}{I_{Li(2s)} + I_{HF}} \frac{Q_{Li,HF}}{Q_{Li,HF}^7 + S_{11,HF}^7}$$
$$\times \Phi_{11,HF}^{disp}(\mathbf{R}) K_{11,HF}(r_{HF}), \tag{82}$$

where I_A is the ionization potential for species A, α_A is the polarizability of species A, $Q_{Li,HF}$ is the magnitude of the translational Jacobi coordinate, i.e., $Q_{Li,HF} = |\mathbf{Q}_{Li,HF}|$, where $\mathbf{Q}_{Li,HF}$ is the vector from Li to the center of mass of HF. The polarizability of HF includes angular dependence,

$$\alpha_{HF}(\mathbf{R}) = \alpha_{HF}^\perp \sin^2 \chi_{Li,HF} + \alpha_{HF}^\| \cos^2 \chi_{Li,HF}, \tag{83}$$

where $\chi_{Li,HF}$ is Jacobi angle, i.e., the angle between the translational Jacobi vector $\mathbf{Q}_{Li,HF}$ and the diatomic Jacobi vector from H to F. The angular dependence is cut off in the interaction region,

$$\Phi_{11,HF}^{disp}(\mathbf{R}) = 1 + \left([(\tfrac{1}{3}\alpha_{HF}^\perp + \tfrac{2}{3}\alpha_{HF}^\|)/\alpha_{HF}(\mathbf{R})] - 1 \right) \exp[-(Q_{Li,HF}/S_{11,HF})^4]. \tag{84}$$

The dipole-induced-dipole interaction is given by

$$U_{11,HF}^{did}(\mathbf{R}) = -\frac{1}{2}(3\cos^2 \chi_{Li,HF} + 1)\alpha_{Li(2s)}\mu_{HF}(r_{HF})^2 \frac{Q_{Li,HF}}{Q_{Li,HF}^7 + S_{11,HF}^7}$$
$$\times \Phi_{11,HF}^{did}(\mathbf{R}) K_{11,HF}(r_{HF}), \tag{85}$$

where the angular dependence is cut off in the interaction region,

$$\Phi_{11,HF}^{did}(\mathbf{R}) = 1 + \left([5/2(3\cos^2 \chi_{Li,HF} + 1)] - 1 \right) \exp[-(Q_{Li,HF}/S_{11,HF})^4], \tag{86}$$

and the dipole moment of HF, μ_{HF}, is taken from Ref. 11. Both long-range interactions are cut off for large values of r_{HF},

$$K_{11,HF}(r_{HF}) = \frac{1}{2} - \frac{1}{2}\tanh[(r_{HF} - r^0_{11,HF})/\Delta_{11,HF}]. \tag{87}$$

The U_{22} surface contains the dipole-quadrupole, quadrupole-quadrupole, dipole-induced-dipole, and dispersion interactions in the Li(2p) + HF arrangement, and the dipole-induced-dipole and dispersion interactions in the LiF + H arrangement,

$$U^{LR}_{22}(\mathbf{R}) = U^{dq}_{22,HF}(\mathbf{R}) + U^{qq}_{22,HF}(\mathbf{R}) + U^{disp}_{22,HF}(\mathbf{R}) + U^{did}_{22,HF}(\mathbf{R})$$
$$+ U^{disp}_{22,LiF}(\mathbf{R}) + U^{did}_{22,LiF}(\mathbf{R}). \tag{88}$$

The dipole-quadrupole interaction is given by

$$U^{dq}_{22,HF}(\mathbf{R}) = \frac{3}{4}\mu_{HF}(r_{HF})\Theta_{Li(2p)} \cos\chi_{Li,HF} \frac{Q_{Li,HF}}{Q^5_{Li,HF} + S^5_{22,HF}}$$
$$\times \Phi^{dq}_{22,HF}(\mathbf{R})K_{22,HF}(r_{HF}), \tag{89}$$

where Θ_A is the quadrupole moment of species A. The angular dependence of the dipole-quadrupole interaction is cut off in the interaction region,

$$\Phi^{dq}_{22,HF}(\mathbf{R}) = \exp[-(Q_{Li,HF}/S_{22,HF})^4]. \tag{90}$$

The quadrupole-quadrupole interaction is given by

$$U^{qq}_{22,HF}(\mathbf{R}) = \frac{3}{4}\Theta_{HF}(r_{HF})\Theta_{Li(2p)}(3 - 7\cos^2\chi_{Li,HF})\frac{Q_{Li,HF}}{Q^6_{Li,HF} + S^6_{22,HF}}$$
$$\times \Phi^{qq}_{22,HF}(\mathbf{R})K_{22,HF}(r_{HF}), \tag{91}$$

where the quadrupole moment of HF is dependent on r_{HF} and is taken from Ref. 12. The angular dependence of the dipole-quadrupole interaction is cut off in the interaction region,

$$\Phi^{qq}_{22,HF}(\mathbf{R}) = 1 - [1/(6 - 14\cos^2\chi_{Li,HF}) + 1]\exp[-(Q_{Li,HF}/S_{22,HF})^4]. \tag{92}$$

The dispersion interaction is given by the London equation,

$$U_{22,\text{HF}}^{\text{disp}}(\mathbf{R}) = -\frac{3}{2}\frac{I_{\text{Li}(2p)}I_{\text{HF}}\alpha_{\text{Li}(2p)}(\mathbf{R})\alpha_{\text{HF}}(\mathbf{R})}{I_{\text{Li}(2p)} + I_{\text{HF}}}\frac{Q_{\text{Li},\text{HF}}}{Q_{\text{Li},\text{HF}}^7 + S_{22,\text{HF}}^7} \tag{93}$$
$$\times \Phi_{22,\text{HF}}^{\text{disp}}(\mathbf{R})K_{22,\text{HF}}(r_{\text{HF}}),$$

The polarizability of Li(2p) includes angular dependence,

$$\alpha_{\text{Li}(2p)}(\mathbf{R}) = \alpha_{\text{Li}(2p)}^{\perp}\sin^2\chi_{\text{Li},\text{HF}} + \alpha_{\text{Li}(2p)}^{\|}\cos^2\chi_{\text{Li},\text{HF}}. \tag{94}$$

The angular dependence is cut off in the interaction region,

$$\Phi_{22,\text{HF}}^{\text{disp}}(\mathbf{R}) = \left\|\left[\tfrac{1}{3}\alpha_{\text{HF}}^{\perp} + \tfrac{2}{3}\alpha_{\text{HF}}^{\|}\right]\left[\tfrac{1}{3}\alpha_{\text{Li}(2p)}^{\perp} + \tfrac{2}{3}\alpha_{\text{Li}(2p)}^{\|}\right]/\left[\alpha_{\text{HF}}(\mathbf{R})\alpha_{\text{Li}(2p)}(\mathbf{R})\right]\right) - 1\right|$$
$$\times \exp[-(Q_{\text{Li},\text{HF}}/S_{22,\text{HF}})^4] + 1. \tag{95}$$

The dipole-induced-dipole interaction is given by

$$U_{22,\text{HF}}^{\text{did}}(\mathbf{R}) = -\frac{1}{2}(3\cos^2\chi_{\text{Li},\text{HF}} + 1)\alpha_{\text{Li}(2p)}(\mathbf{R})\mu_{\text{HF}}(r_{\text{HF}})^2\frac{Q_{\text{Li},\text{HF}}}{Q_{\text{Li},\text{HF}}^7 + S_{22,\text{HF}}^7} \tag{96}$$
$$\times \Phi_{22,\text{HF}}^{\text{did}}(\mathbf{R})K_{22,\text{HF}}(r_{\text{HF}}),$$

where the angular dependence is cut off in the interaction region,

$$\Phi_{22,\text{HF}}^{\text{did}}(\mathbf{R}) = 1 + \left(\left[5\left[\tfrac{1}{3}\alpha_{\text{Li}(2p)}^{\perp} + \tfrac{2}{3}\alpha_{\text{Li}(2p)}^{\|}\right]/\left[2\alpha_{\text{Li}(2p)}(\mathbf{R})(3\cos^2\chi_{\text{Li},\text{HF}} + 1)\right]\right] - 1\right)$$
$$\times \exp[-(Q_{\text{Li},\text{HF}}/S_{11,\text{HF}})^4]. \tag{97}$$

The Li(2p) + HF long-range interactions are cut off for large values of r_{HF},

$$K_{22,\text{HF}}(r_{\text{HF}}) = \frac{1}{2} - \frac{1}{2}\tanh[(r_{\text{HF}} - r_{22,\text{HF}}^0)/\Delta_{22,\text{HF}}]. \tag{98}$$

The dispersion interaction in the LiF + H arrangement is given by the London equation,

$$U_{22,\text{LiF}}^{\text{disp}}(\mathbf{R}) = -\frac{3}{2}\frac{I_{\text{LiF}}I_{\text{H}}\alpha_{\text{LiF}}\alpha_{\text{H}}}{I_{\text{LiF}} + I_{\text{H}}}\frac{K_{22,\text{LiF}}(r_{\text{LiF}})}{Q_{\text{H},\text{LiF}}^6 + S_{22,\text{LiF}}^6}, \tag{99}$$

where $Q_{\text{H},\text{LiF}}$ is the magnitude of the translational Jacobi coordinate in the LiF + H arrangement, i.e., $Q_{\text{H},\text{LiF}}$ is the magnitude of the vector from H to the center of mass of LiF. The masses of Li and F are therefore parameters of the fit are given in Table 1. The dipole-induced-dipole interaction is given by

$$U_{22,\text{LiF}}^{\text{did}}(\mathbf{R}) = -\frac{1}{2}\frac{(3\cos^2\chi_{\text{H,LiF}}+1)\alpha_{\text{H}}\mu_{\text{LiF}}(r_{\text{LiF}})^2}{Q_{\text{H,LIF}}^6 + S_{22,\text{LiF}}^6}\Phi_{22,\text{LiF}}^{\text{did}}(\mathbf{R})K_{22,\text{LiF}}(r_{\text{LiF}}), \quad (100)$$

where $\chi_{\text{H,LiF}}$ is Jacobi angle in the LiF + H arrangement, i.e., the angle between the translational Jacobi vector $\mathbf{Q}_{\text{H,LiF}}$ and the diatomic Jacobi vector from Li to F. The dipole moment of LiF is based on the data in Ref. 13 and is given by

$$\mu_{\text{LiF}} = \mu_{\text{LiF}}^{\text{D}}\exp[-\mu_{\text{LiF}}^{\alpha}(r_{\text{LiF}}-\mu_{\text{LiF}}^r)^2], \quad (101)$$

$$\mu_{\text{LiF}}^{\alpha}(r_{\text{LiF}}) = \mu_{\text{LiF}}^{\alpha 0} + \mu_{\text{LiF}}^{\alpha 1}m_{\text{LiF}}(r_{\text{LiF}}) + \mu_{\text{LiF}}^{\alpha 8}m_{\text{LiF}}(r_{\text{LiF}})^8, \quad (102)$$

$$m_{\text{LiF}} = r_{\text{LiF}} - m_{\text{LiF}}^0. \quad (103)$$

The angular dependence is cut off in the interaction region,

$$\Phi_{22,\text{LiF}}^{\text{did}}(\mathbf{R}) = 1 + \big([5/(3\cos^2\chi_{\text{H,LiF}}+1)]-1\big)\exp[-(Q_{\text{H,LiF}}/S_{22,\text{LiF}})^4]. \quad (104)$$

The LiF + H long-range interactions are cut off for large values of r_{LiF},

$$K_{22,\text{LiF}}(r_{\text{LiHF}}) = \frac{1}{2} - \frac{1}{2}\tanh[(r_{\text{LiF}}-r_{22,\text{LiF}}^0)/\Delta_{22,\text{LiF}}]. \quad (105)$$

The parameters used for the long-range interactions are given in Table 4.

3. Quasidiabatic potential energy matrix for LiFH: Surface fit JS

The surface fit described in Sec. 2 (surface fit J) is our most accurate fit to the LiFH *ab initio* data. Surface fit J contains long-range interactions that are based on physically motivated functional forms and that depend on physical properties such as the polarizabilities and multipole moments of the H and Li atoms and of the HF and LiF molecules. We believe that surface fit J is extremely accurate; however, the presence of long-range forces may increase the computational effort required to obtain converged nuclear dynamics for both quantum mechanical and semiclassical simulations. We therefore present as a complement to surface fit J, surface fit JS, which features cut-off long-range forces. The long-range forces were cut off in such a way as to minimize the change to the interaction region, as discussed below. We also carefully cut off the diabatic coupling U_{12} in surface fit JS. The diabatic coupling is cut off in a region where the coupling is not expected to play a significant role in the dynamics, and this feature also decreases the difficulty of dynamics calculations.

The diagonal quasidiabatic matrix elements of surface fit JS (U_{11}^{JS} and U_{22}^{JS}) are identical to those of surface fit J, except that the long-range terms are cut off,

$$U_{ii}^{JS}(\mathbf{R}) = U_{ii}^{I}(\mathbf{R}) + U_{ii}^{JS}(\mathbf{R}), \tag{106}$$

$$U_{11}^{JS}(\mathbf{R}) = U_{11}^{LR}(\mathbf{R})\Omega(Q_{Li,HF}), \tag{107}$$

$$U_{22}^{JS}(\mathbf{R}) = \left[U_{22,HF}^{dq}(\mathbf{R}) + U_{22,HF}^{qq}(\mathbf{R}) + U_{22,HF}^{disp}(\mathbf{R}) + U_{22,HF}^{did}(\mathbf{R}) \right] \Omega(Q_{Li,HF})$$
$$+ \left[U_{22,LiF}^{disp}(\mathbf{R}) + U_{22,LiF}^{did}(\mathbf{R}) \right]\Omega(Q_{H,LiF}), \tag{108}$$

where $i = 1$ and 2, $Q_{A,BC}$ is the magnitude of the translational Jacobi coordinate in the A + BC molecular arrangement, and the interaction potential $U_{ii}^{I}(\mathbf{R})$ and the long-range forces are the same as those that were given for surface fit J in Sec. 2. The cut off functions are

$$\Omega(Q_{A,BC}) = \begin{cases} \exp[\Delta_{\Omega}/(Q_{A,BC} - Q_{\Omega})] & Q_{A,BC} \leq Q_{\Omega} \\ 0 & Q_{A,BC} > Q_{\Omega}, \end{cases} \tag{109}$$

where "A,BC" is "Li,HF" or "H,LiF". Note that the cut off function in Eq. (109) goes exactly to zero at Q_{Ω} and has an infinite number of continuous derivatives for all

$Q_{A,BC}$. The values for the cut off parameters are $Q_\Omega = 10.0$ a_0 and $\Delta_\Omega = 0.2$ a_0. These values were optimized such that surface fit JS remained smooth and the mean unsigned errors calculated for surface fit JS were no more than 0.001 eV greater than those reported for surface fit J in Table VIII of the main paper.

The diabatic coupling (U_{12}^{JS}) was also cut off in surface fit JS,

$$U_{12}^{JS}(\mathbf{R}) = U_{12}(\mathbf{R})\Xi(r_{HF}),\tag{110}$$

where U_{12} is the diabatic coupling of surface fit J and is given in Sec. 2, and

$$\Xi(r_{HF}) = \frac{1}{2} - \frac{1}{2}\tanh[(r_{HF} - r_\Xi)/\Delta_\Xi].\tag{111}$$

The parameters for the cut off function are $r_\Xi = 5.5$ a_0 and $\Delta_\Xi = 0.2$ a_0. This cut off function does not significantly effect the mean unsigned errors for surface fit JS.

4. References

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5. Tables

TABLE 1. Values of the parameters used in the LiFH U_{11} potential energy function.

Parameter	Value	Parameter	Value
D_{LiH}^a	12.93744 eV	r_{HF}^0	2.1042 a_0
D_{LiH}^c	11.09130 eV	r_{HF}^c	1.6739 a_0
β_{LiH}^a	1.80587 a_0^{-1}	β_{HF}^c	0.74633 a_0^{-1}
β_{LiH}^c	1.21114 a_0^{-1}	D_{HF}^{cc}	0.86608 eV
r_{LiH}^0	1.34321 a_0	D_{HF}^{chi}	0.34457 eV
ρ_{LiH}	1.07143 a_0	ρ_{HF}	1.63 a_0
Δ_{LiH}	0.6 a_0	Δ_{HF}	2.9941 a_0
$\varkappa_{LiH}$	0.4	D_{LiF}	0.17427 eV
D_{HF}^e	6.122 eV	β_{LiF}	1.49062 a_0^{-1}
r_{HF}^e	1.733 a_0	r_{LiF}^0	3.6 a_0
b_{HF}^0	1.1622 a_0^{-1}	m_{Li}	7.016003 amu[a]
b_{HF}^1	–0.025647 a_0^{-2}	m_F	18.998403 amu
b_{HF}^2	0.059062 a_0^{-3}	m_H	1.007825 amu

[a] 1 amu = 1822.887 m_e.

TABLE 2. Values of the parameters used in the LiFH U_{12} potential energy function.

Parameter	Value	Parameter	Value
ρ_{12}	4.87097 a_0	$\rho_{HF,2}$	1.45161 a_0
Δ_{12}	2.0 a_0	$\Delta_{HF,1}$	1.75806 a_0
g_{LiH}	1.27742 eV	$\Delta_{HF,2}$	0.98387 a_0
g_{LiF}	0.48 eV	ρ_{LiF}	2.00098 a_0
r^0_{LiH}	3.00489 a_0	Δ_{LiF}	0.90626 a_0
r^0_{LiF}	3.49756 a_0	ρ_{LiH}	4.98436 a_0
$\rho_{HF,1}$	1.15484 a_0	Δ_{LiH}	2.08993 a_0

TABLE 3. Values of the parameters used in the LiFH U_{22} potential energy function.

Parameter	Value	Parameter	Value
c_{2a}	3.5 eV	$D_{HF}^{t1,180}$	4.56304985 eV
c_{2b}	0.27362 eV^{-2}	$\beta_{HF}^{t,0}$	2.4105572 a_0^{-1}
c_{2c}	0.15 a_0^{-1}	$\beta_{HF}^{t,180}$	1.4046921 a_0^{-1}
D_{LiH}^{a2}	4.32258 eV	r_{HF}^{t}	1.61329423 a_0
D_{LiH}^{a1}	7.06452 eV	D_{LiF}^{e}	5.947 eV
β_{LiH}^{a}	1.36 a_0^{-1}	r_{LiF}^{e}	2.9553 a_0
D_{LiH}^{c}	14.74194 eV	ρ_{LiF}^{a}	13.0 a_0
β_{LiH}^{c}	0.90667 a_0^{-1}	Δ_{LiF}^{a}	0.5 a_0
r_{LiH}^{0}	1.2 a_0	d_{LiF}^{aa}	1.0243998
ρ_{LiH}	0.72 a_0	ρ_{LiF}^{aa}	3.340762 a_0
Δ_{LiH}	0.5 a_0	Δ_{LiF}^{aa}	0.56353861 a_0
γ_{LiH}	1.0	$\varkappa_{LiF}$	4.6304985 $a_0^{1+1/n_{LiF}}$
D_{LiH}^{t2}	1.1935483 eV	n_{LiF}	8.0
D_{LiH}^{t1}	13.548387 eV	β_{LiF}^{d}	0.13225806 a_0^{-1}
β_{LiH}^{t}	2.41319648 a_0^{-1}	ρ_{LiF}^{b}	3.382209 a_0
r_{LiH}^{t}	1.203323 a_0	Δ_{LiF}^{b}	0.4947214 a_0^{-1}
D_{HF}^{e}	6.122 eV	b_{LiF}^{e1}	0.064076 a_0^{-1}
$E_{Li(2p)}$	1.848 eV	b_{LiF}^{e2}	103.57
r_{HF}^{e}	1.733 a_0	b_{LiF}^{e3}	4.6498 a_0^2
b_{HF}^{0}	1.1622 a_0^{-1}	b_{LiF}^{e4}	7.0489 a_0

b_{HF}^1	-0.025647 a_0^{-2}	$D_{LiF}^{c,0}$	5.5904203 eV
b_{HF}^2	0.059062 a_0^{-3}	$D_{LiF}^{c,180}$	2.352884 eV
r_{HF}^0	2.1042 a_0	$\beta_{LiF}^{c,0}$	0.7795699 a_0^{-1}
D_{HF}^{aa}	2.3841642 eV	$\beta_{LiF}^{c,180}$	0.8196480 a_0^{-1}
β_{HF}^{aa}	1.799609 a_0^{-1}	ρ_{LiF}^0	0.2017595 a_0
r_{HF}^{aa}	1.60215 a_0	ρ_{LiF}^{180}	2.0 a_0
ρ_{HF}^a	3.0 a_0	ϕ_{LiF}^0	0.12463343 rad
Δ_{HF}^a	0.5 a_0	ϕ_{LiF}^{180}	0.14907135 rad
D_{HF}^{cc}	0.72629521 eV	Δ_{LiF}^0	0.51710655 a_0^{-1}
D_{HF}^{chi}	0.0486803519 eV	Δ_{LiF}^{180}	0.43695014 a_0^{-1}
ρ_{HF}^c	2.2 a_0	$D_{LiF}^{t2,0}$	-0.0552298 eV
Δ_{HF}^c	0.5 a_0	$D_{LiF}^{t1,0}$	1.8729228 eV
ρ_{HF}	1.00293 a_0	$D_{LiF}^{t2,180}$	0.94662756 eV
Δ_{HF}	4.0899 a_0	$D_{LiF}^{t1,180}$	0.2994134 eV
$D_{HF}^{t2,0}$	1.4242424 eV	$\beta_{LiF}^{t,0}$	0.9519061 a_0^{-1}
$D_{HF}^{t1,0}$	14.203323 eV	$\beta_{LiF}^{t,180}$	0.4531769 a_0^{-1}
$D_{HF}^{t2,180}$	6.15835777 eV		

TABLE 4. Values of the parameters used in the long-range interactions.

Parameter	Value	Parameter	Value
$I_{Li(2s)}$	5.392 eV[a]	$\Delta_{22,HF}$	2.0 a_0
I_{HF}	16.044 eV[a]	I_{LiF}	11.3 eV [a]
$\alpha_{Li(2s)}$	165.0 a_0^3[b]	I_H	13.598 eV [a]
$S_{11,HF}$	6.0 a_0	α_{LiF}	72.9 a_0^3[a]
$\alpha_{HF}^{\perp}$	4.59 a_0^3 [c]	α_H	4.4997 a_0^3[a]
$\alpha_{HF}^{\parallel}$	5.10 a_0^3 [c]	$S_{22,LiF}$	7.0 a_0
$r_{11,HF}^0$	3.0 a_0	μ_{LiF}^D	9.30039 $e\,a_0$
$\Delta_{11,HF}$	2.0 a_0	μ_{LiF}^r	10.4994 a_0
$\Theta_{Li(2p)}$	11.1 $e\,a_0^2$[b]	$\mu_{LiF}^{\alpha 0}$	0.02435 a_0^{-1}
$S_{22,HF}$	6.0 a_0	$\mu_{LiF}^{\alpha 1}$	0.015999 a_0^{-2}
$I_{Li(2p)}$	3.544 eV[a]	$\mu_{LiF}^{\alpha 8}$	9.9355 x 10^{-8} a_0^{-9}
$\alpha_{Li(2p)}^{\perp}$	129.0 a_0^3 [b]	m_{LiF}^0	4.471959 a_0
$\alpha_{Li(2p)}^{\parallel}$	131.0 a_0^3 [b]	$r_{22,LiF}^0$	4.5 a_0
$r_{22,HF}^0$	3.0 a_0	$\Delta_{22,LiF}$	2.0 a_0

[a]Reference 14.

[b]Reference 15.

[c]Reference 16.